Geomicrobiological Treatment for Engineered and Natural Attenuation of Chlorinated Organics

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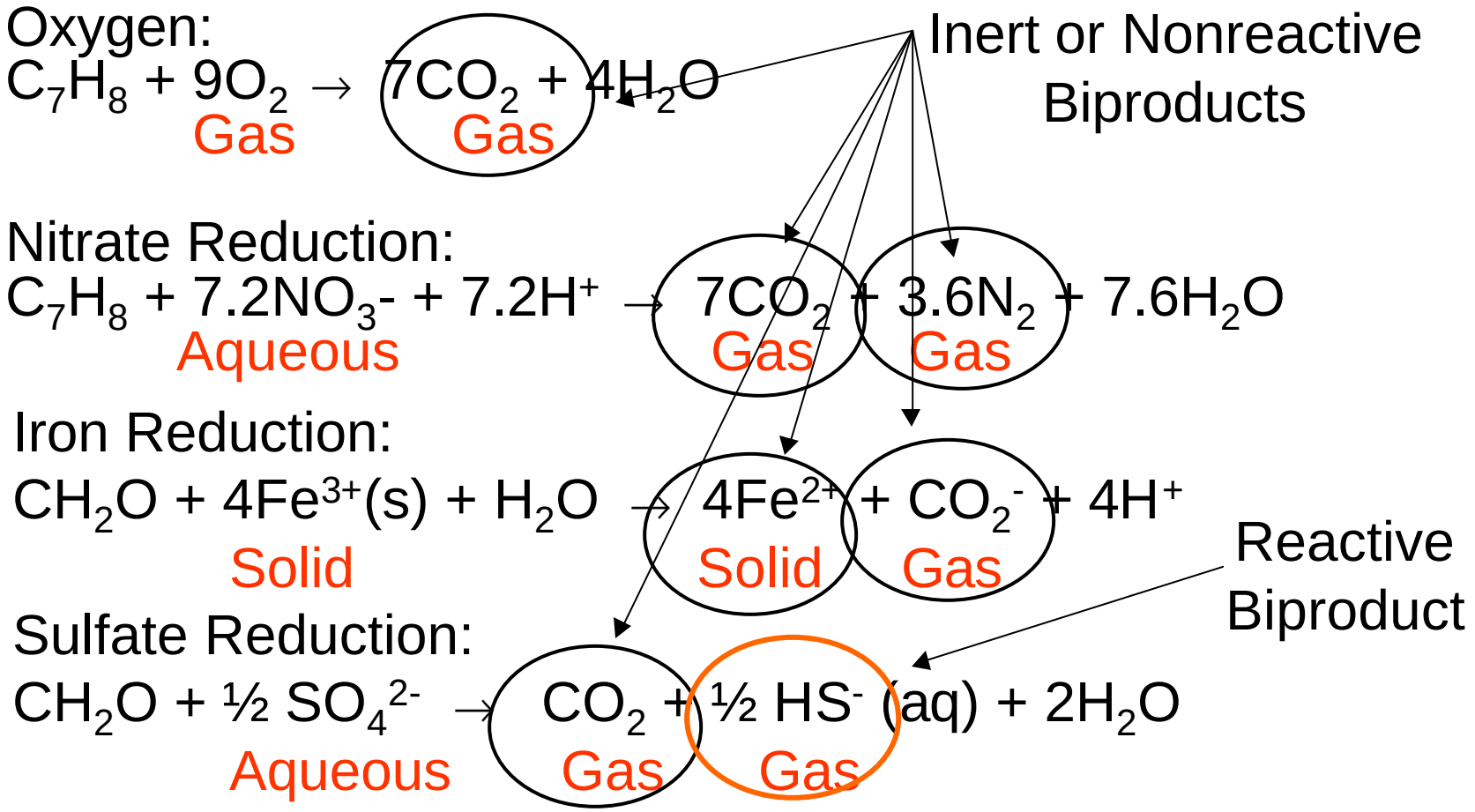
Presentation Objectives

- Review Biogeochemical Process and Theory
  - Enzymatic reductive dechlorination
  - Biogeochemical reductive dechlorination
- Field Observations from Altus AFB
- Laboratory Studies
- Mechanics of Operation and Characteristic Observations
- Advantages and Implementation

Two Principal Routes of Chlorinated Ethene Destruction

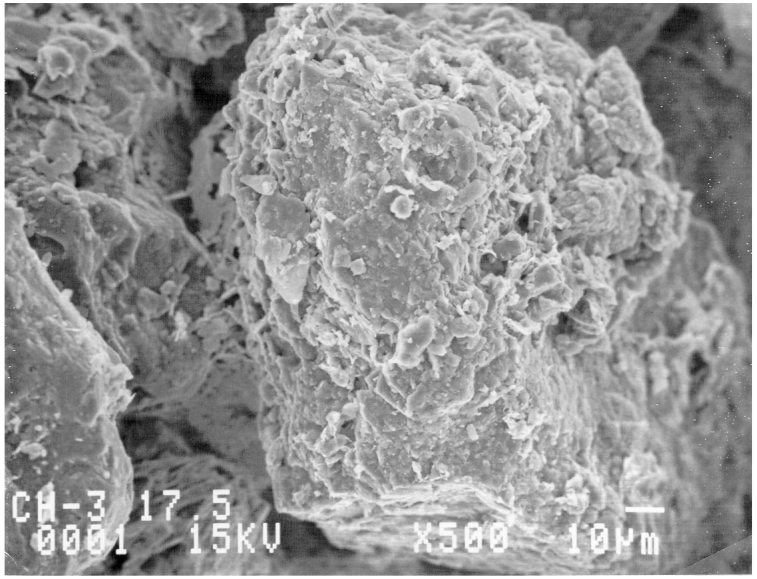
- Enzymatic Reductive Dechlorination (ERD)
  - Bacteria oxidize a labile organic and reduce chlorinated compound directly
- Biogeochemical Reductive Dechlorination (BiRD)
  - Bacteria oxidize a labile organic and reduce aquifer mineral matrix
  - The reduced mineral matrix reduces the chlorinated compound abiotically

Biogeochemical Processes

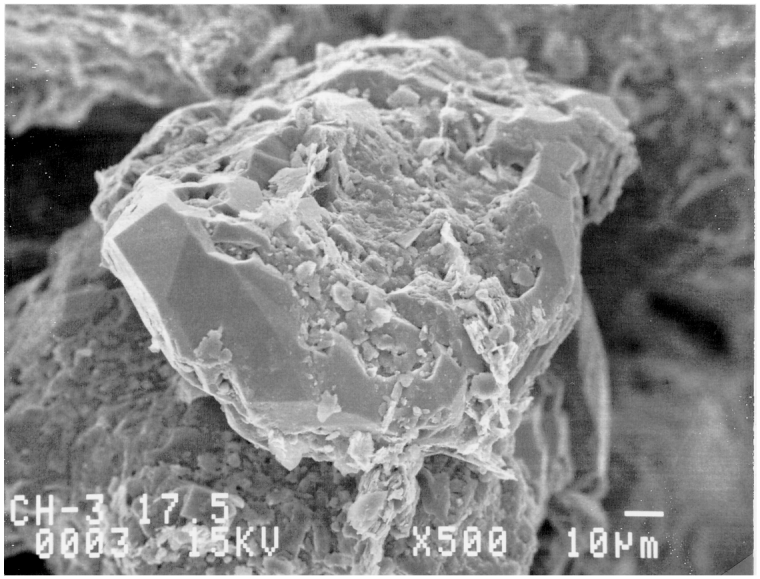


SEM images

Fe^{3+} is solid grain coating and cannot be measured in water

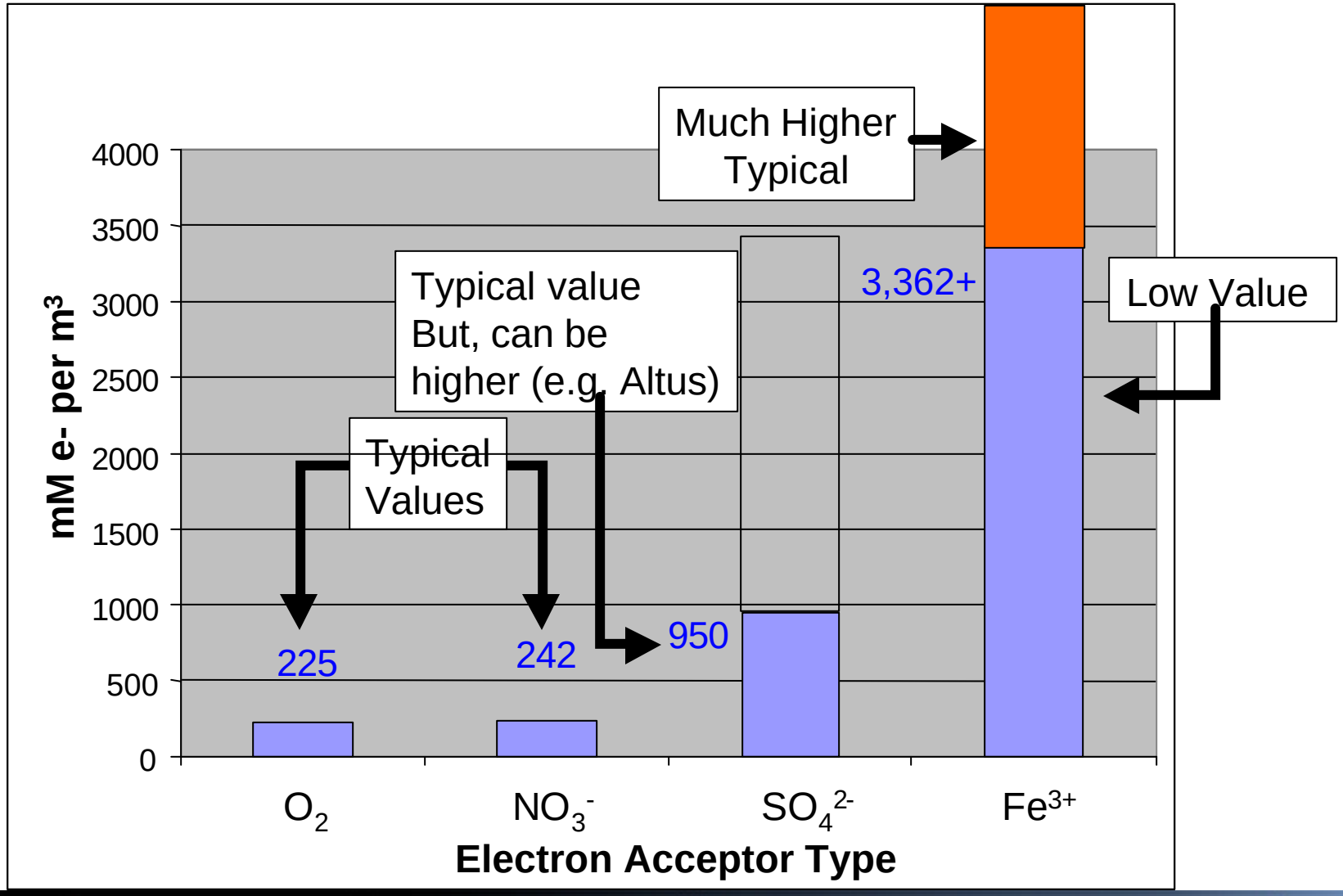


Sand grain in non-contaminated area with iron oxide mineral coating



Sand grain in fuel contaminated area with iron oxide removed and quartz corroded.

Typical Electron Capacity per m^3 Aquifer Material



Sulfate Overall Equations

Reactants Needed to Make FeS

Must be measured in solid matrix not water

$CH_2O + \frac{1}{2} SO_4^{2-} \rightarrow HCO_3 + \frac{1}{2} HS^- (ag) + H_2O + H^+$

$2FeOOH_{(s)} + 3HS^- \rightarrow 2FeS_{(s)} + S^o + H_2O + 3OH^-$

Products Monitored

Highly Reduced And Reactive

$FeS_{(s)} + S^o \rightarrow FeS_{2\ (s)}$

Less Reactive

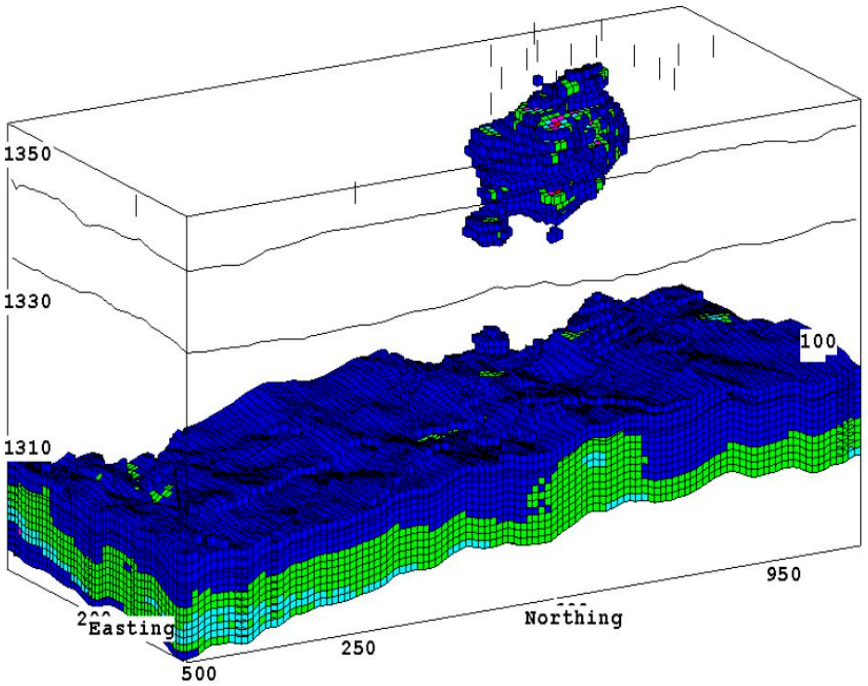
Visible Evidence

Fe and S Mineral Measurements

- Practical methods have been developed to measure:
  - Oxidized Fe^{3+}
  - Reduced FeS, FeS_2, Fe^{2+}
- Aqueous and Mineral

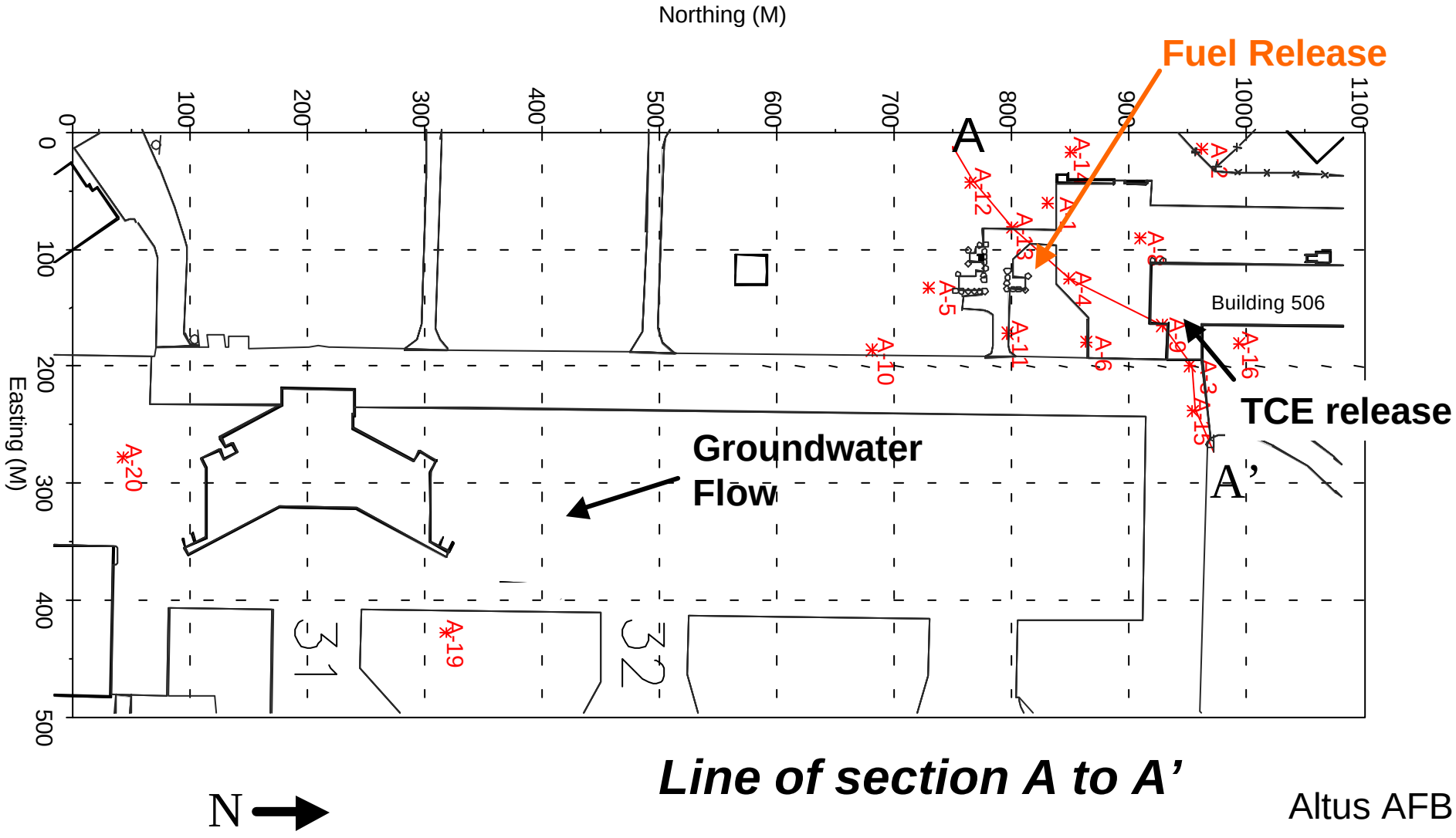
  Intrinsic Bioremediation

  Assessment (AMIBA)
- Usually we model in 3D



Altus AFB 3D model of FeS_2 from fuel leak area.

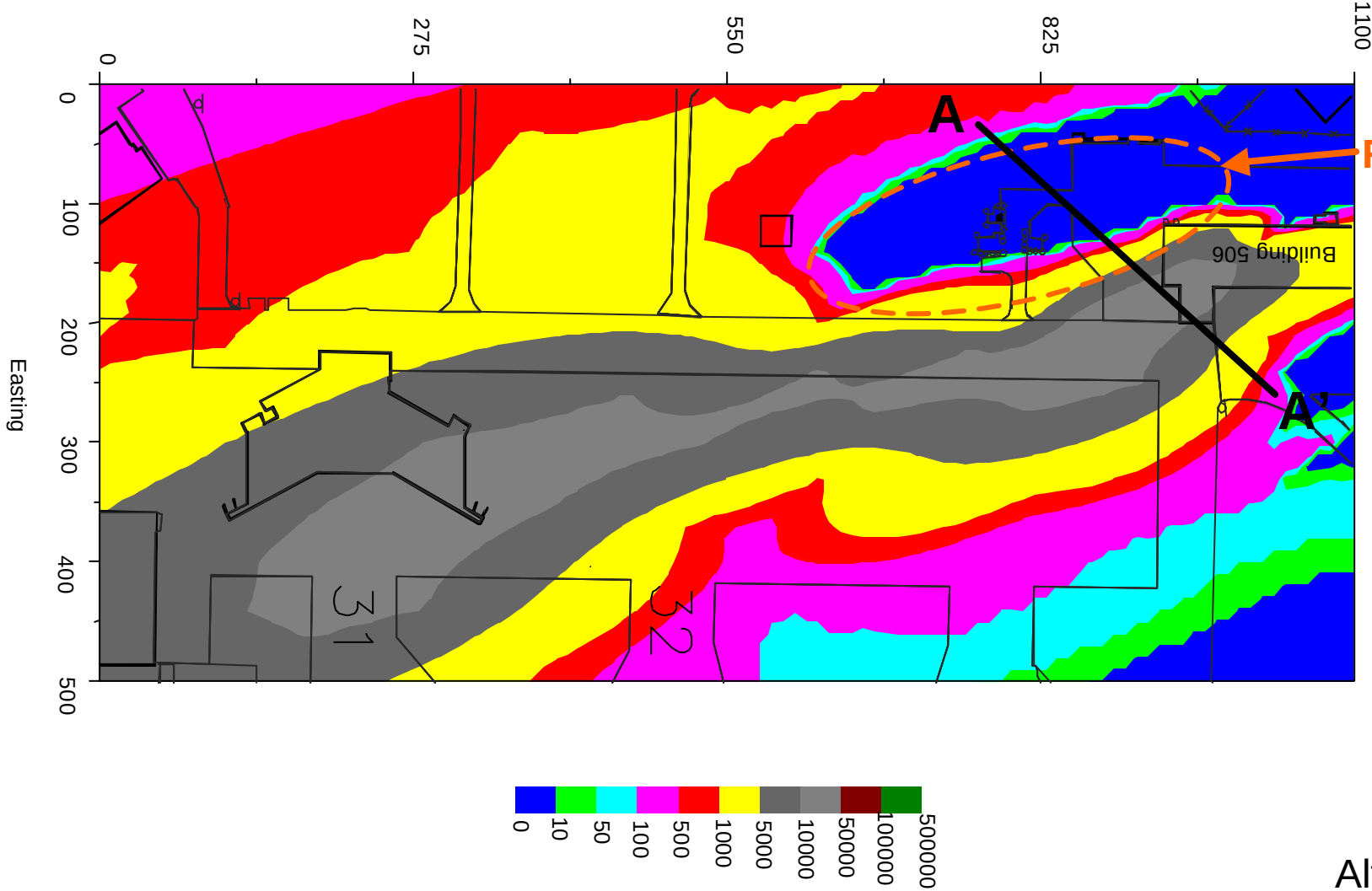
Example from Altus AFB



Line of section A to A'

Altus AFB

Clay aquifer TCE (map plan) relative to fuel release (ug/L)

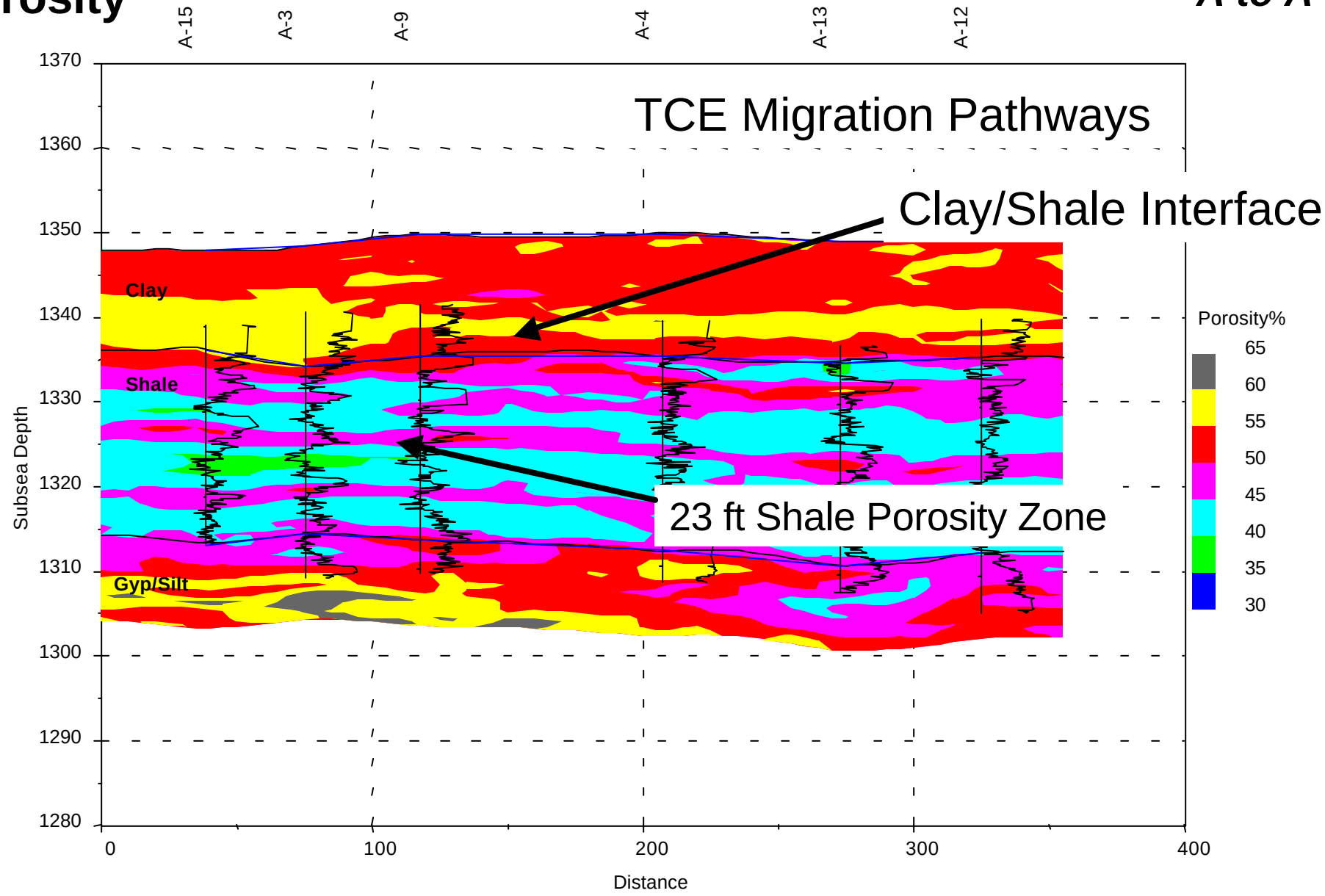


Fuel Release Area

Altus AFB

Porosity

A to A'

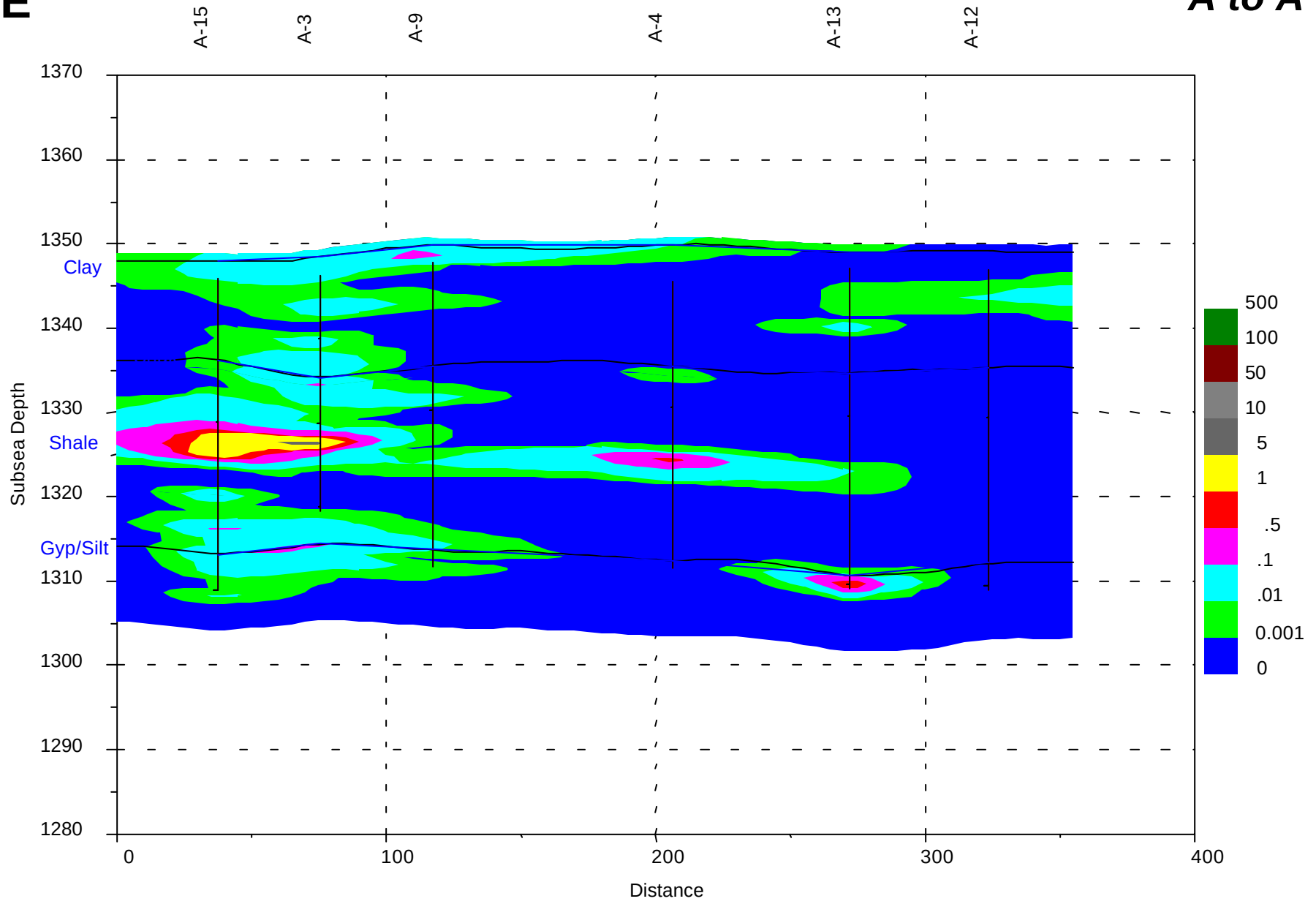


Porosity profile from density log borehole geophysics A to A'

Altus AFB

TCE

A to A'

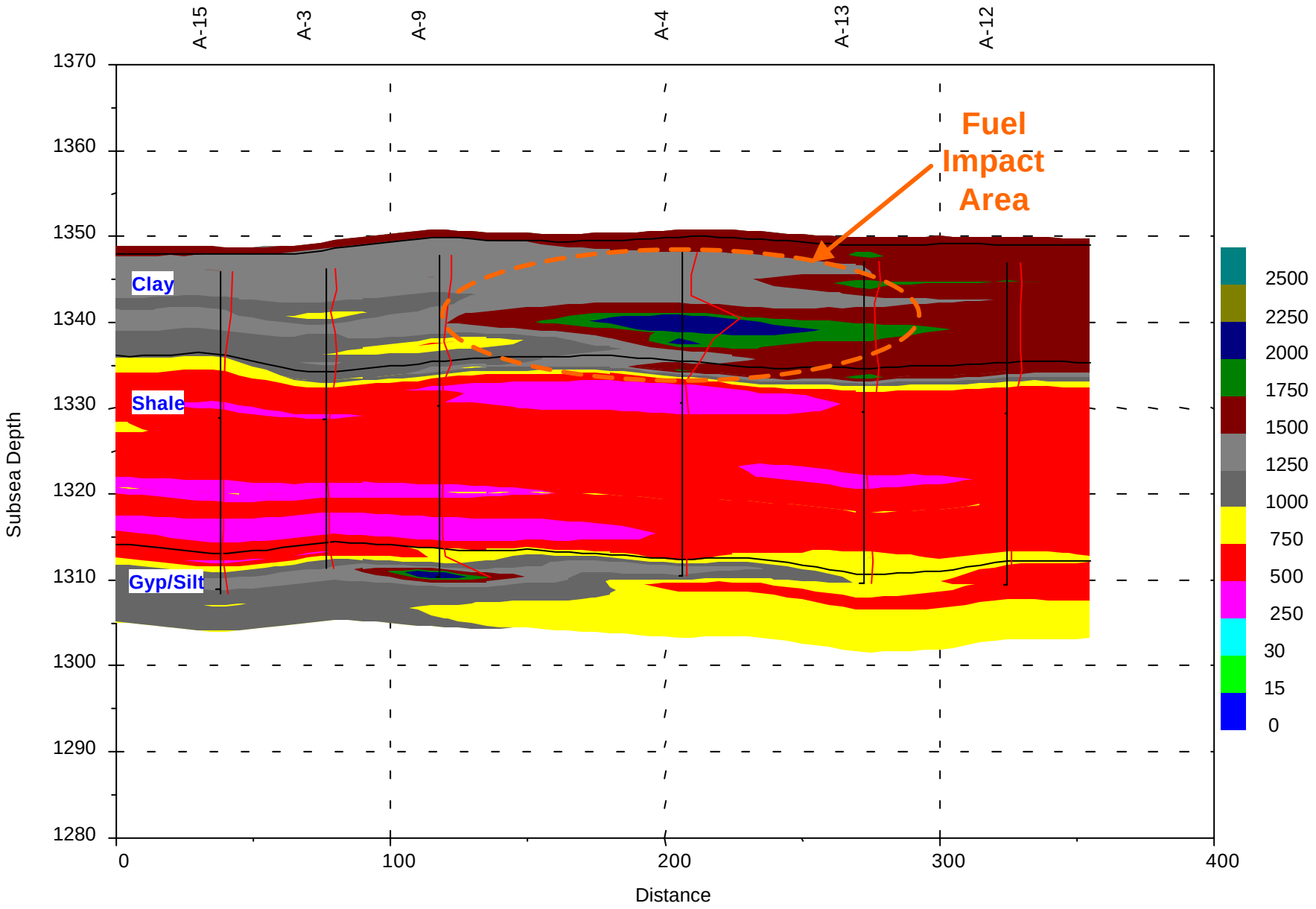


Soil phase TCE along line of section A to A' (ug/Kg)

Altus AFB

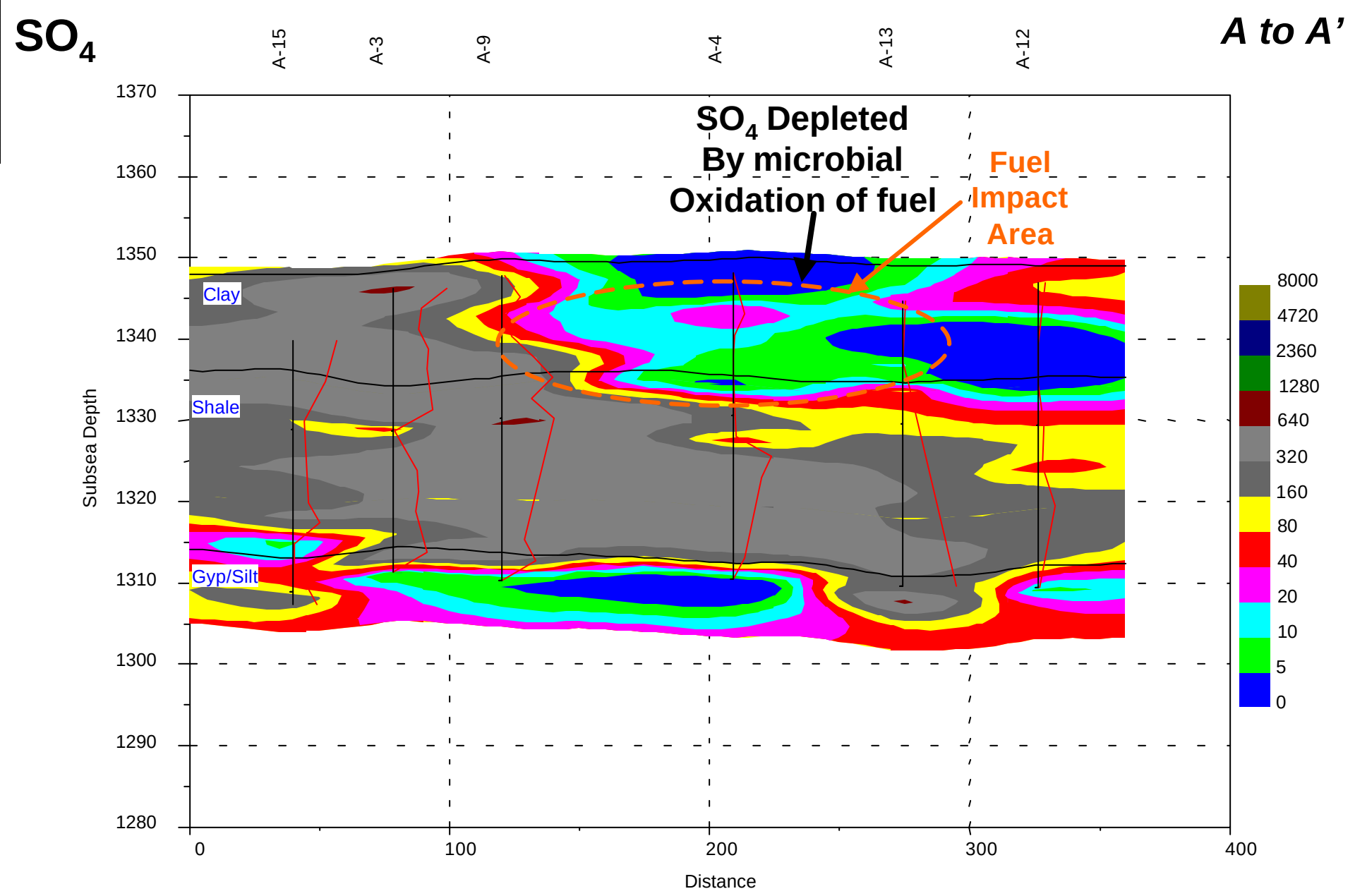
Fe

A to A’



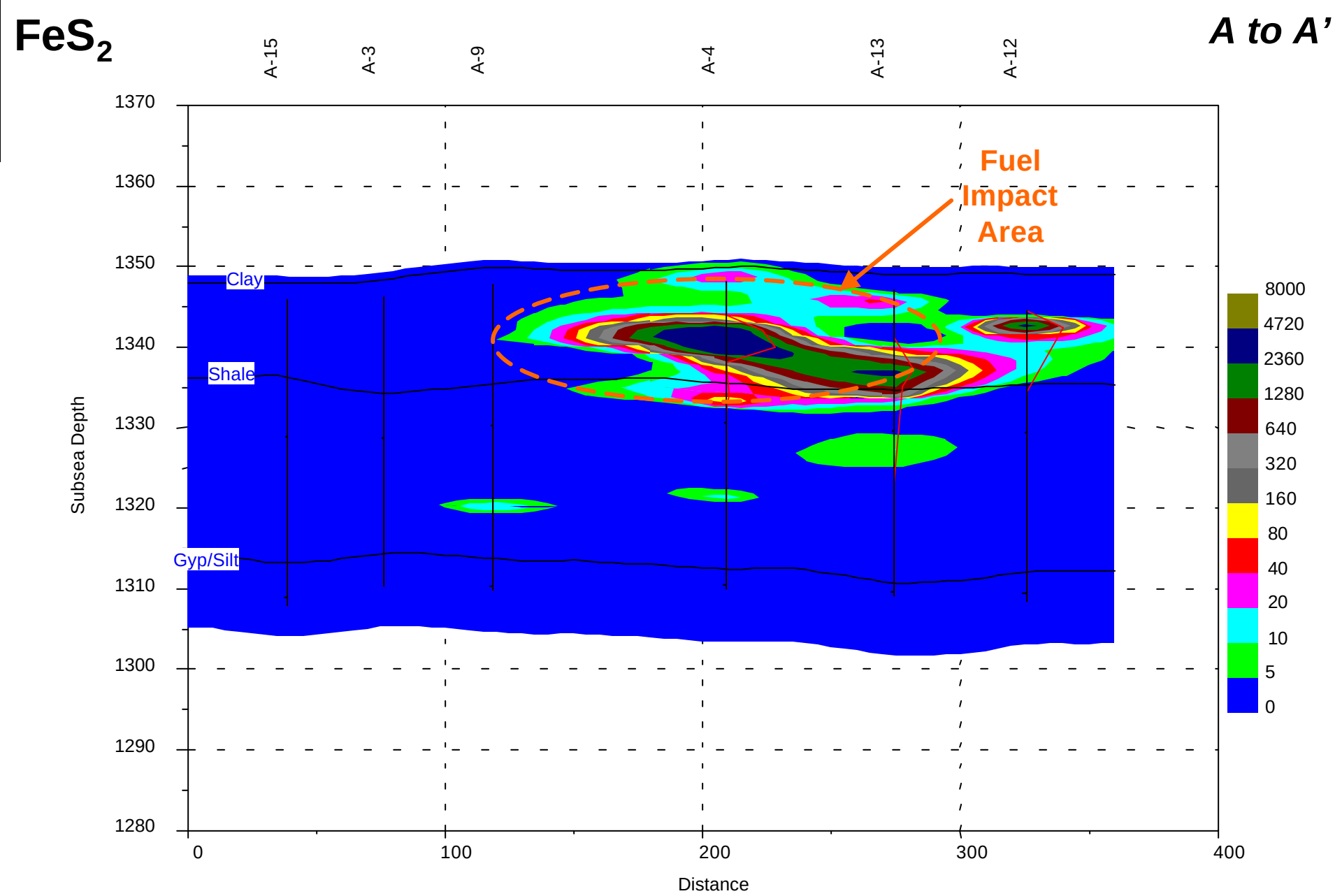
Total reactive iron along profile A to A’ (mg/Kg)

Altus AFB



SO_4 along profile A to A'

Altus AFB

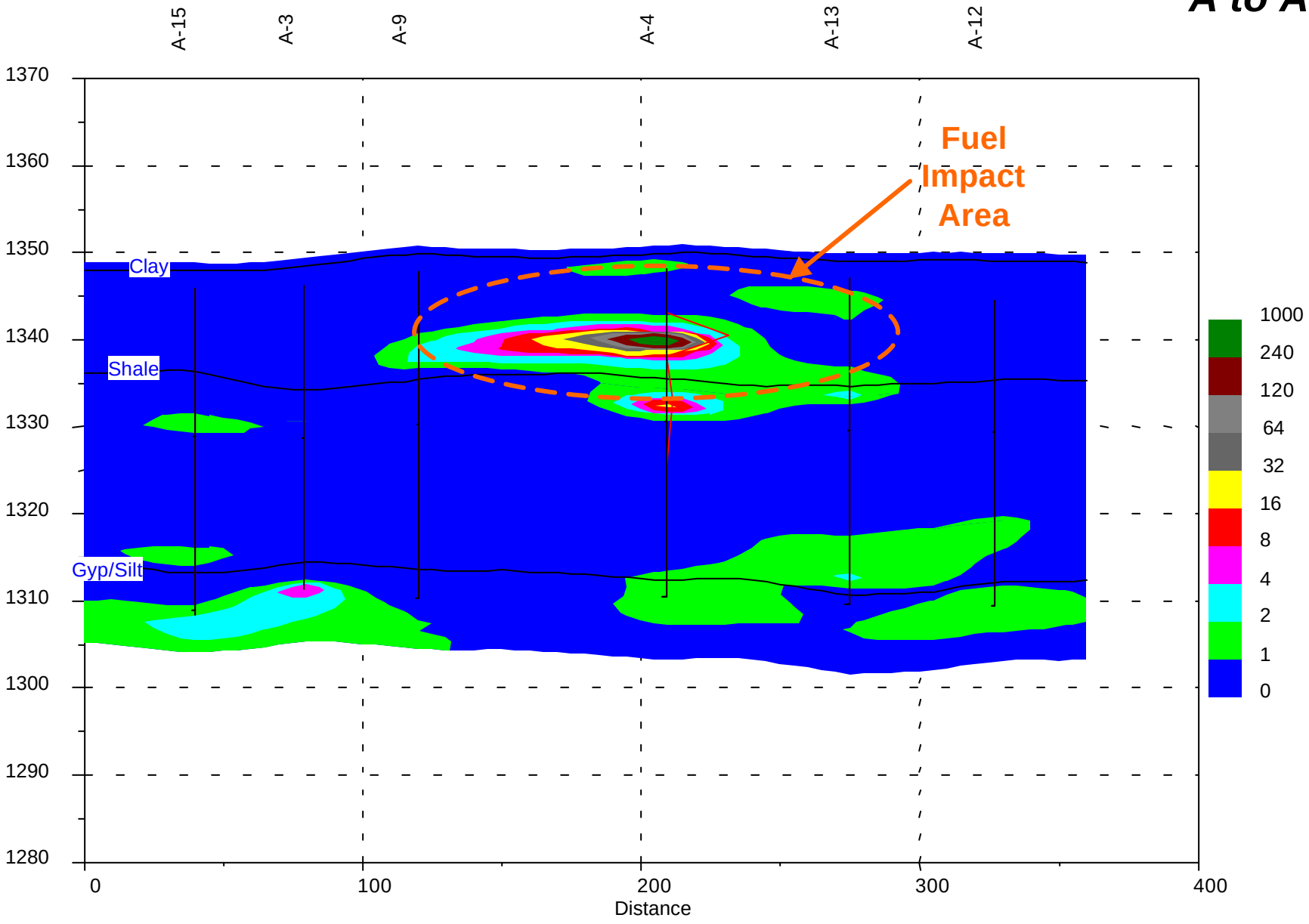


S from FeS_2 along profile A to A' (mg/Kg)

Altus AFB

FeS

A to A'

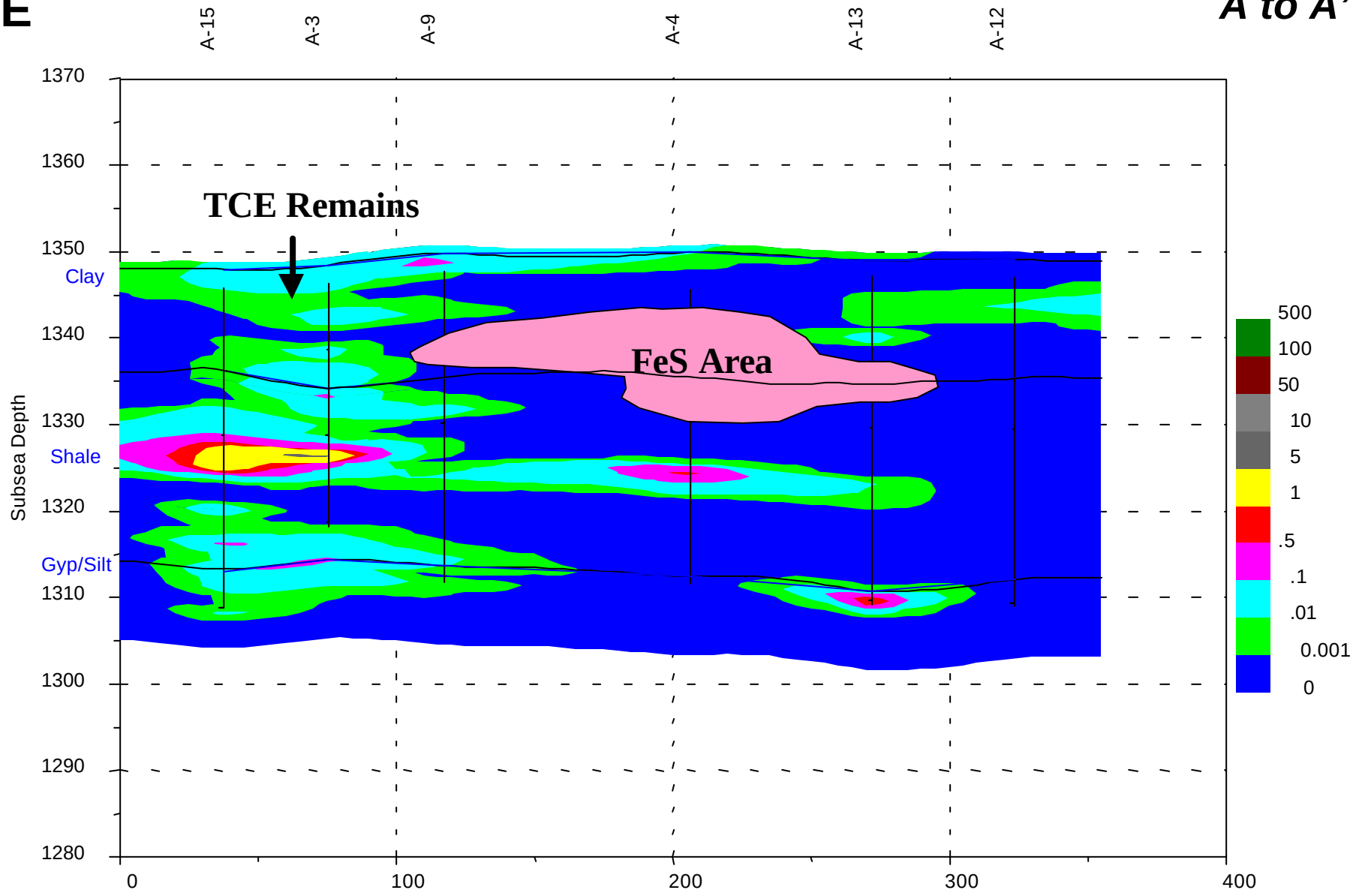


Profile of mineral FeS along line of section A to A' (mg/Kg)

Altus AFB

TCE

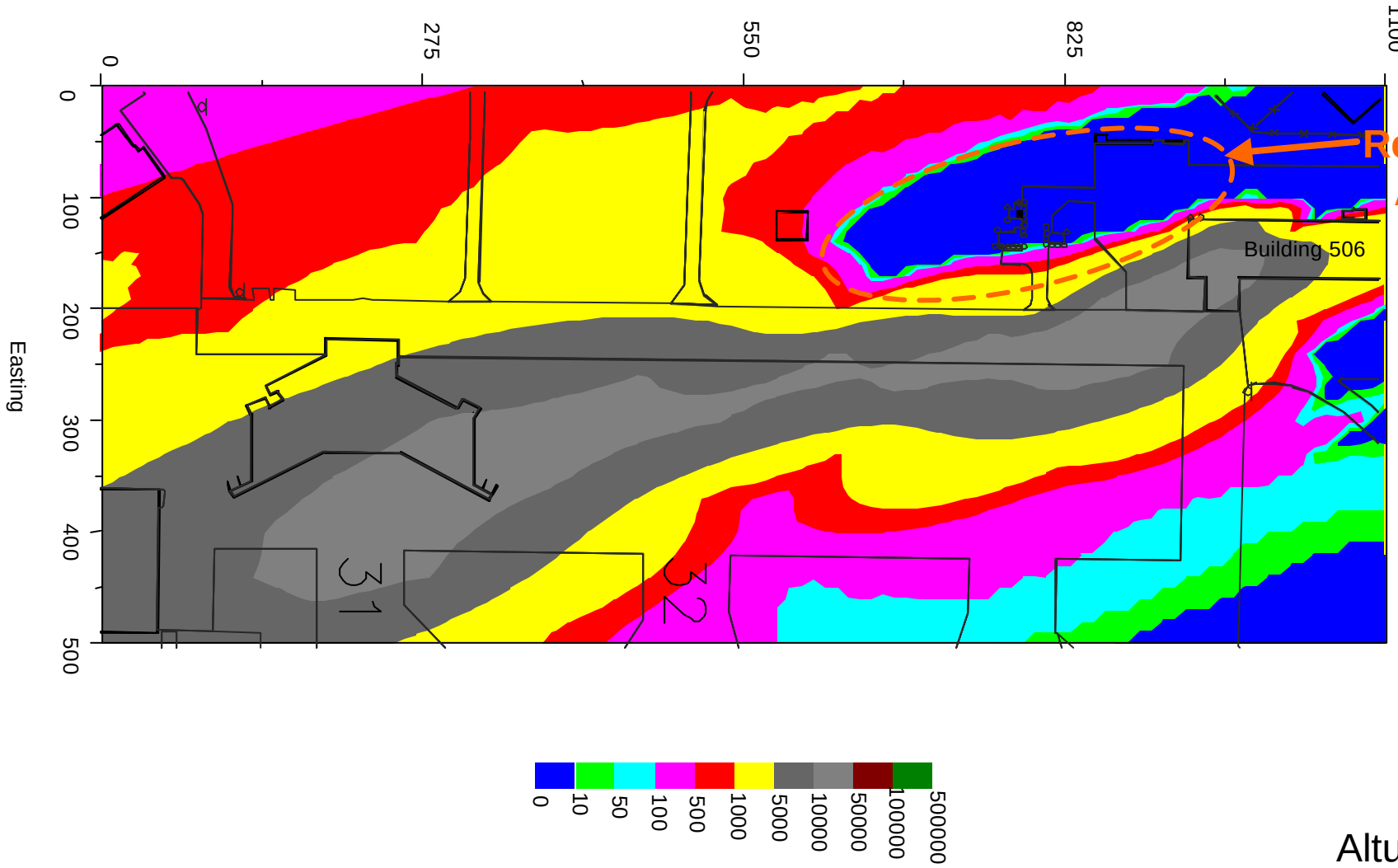
A to A'



Soil phase TCE along A to A' (ug/Kg) with FeS area superimposed

Altus AFB

Clay aquifer TCE (map plan) relative to fuel release (ug/L)



Altus AFB

Mechanics and Characteristic Observations

- ERD
- BiRD

Mechanics of Enzymatic Reductive Dechlorination (ERD)

- Organic added as electron donor to drive aquifer anaerobic
- After oxygen, nitrate, and sulfate reduction, chlorinated ethanes can be used as electron acceptors

First Used → Last Used

Oxygen > Nitrate > Sulfate > Fe^{3+} > Methanogenesis

↑ Chlorinated Ethenes

- Direct enzymatic reduction follows:

$1/6C_2HCl_3 + 1/8CH_3COOH + 1/4H_2O \rightarrow 1/6C_2H_4 + 1/4CO_2 + ½H^+ + ½Cl^-$

Indicators of ERD

- Characteristic observations:
  - Stepwise systematic dechlorination
    - PCE ➔ TCE ➔ DCE ➔ VC ➔ ethene
    - Should see increase in daughter products w/r time or distance down-gradient
- Approach works best in environments low in sulfate

Problems with ERD

- Organic-Contaminant-Bacteria mixing
- Viscous organic plugs permeability
- Chlorinated Ethene reduction not natural
  - No natural analog so no preadapted bacteria
  - Required bacteria not always present
- Long lag time
- Slow reaction kinetics
- Creation of daughter products including VC
- High amount of organic may be required
  - Use up sulfate
  - used for methanogenesis

Mechanics of Biogeochemical Reductive Dechlorination (BiRD)

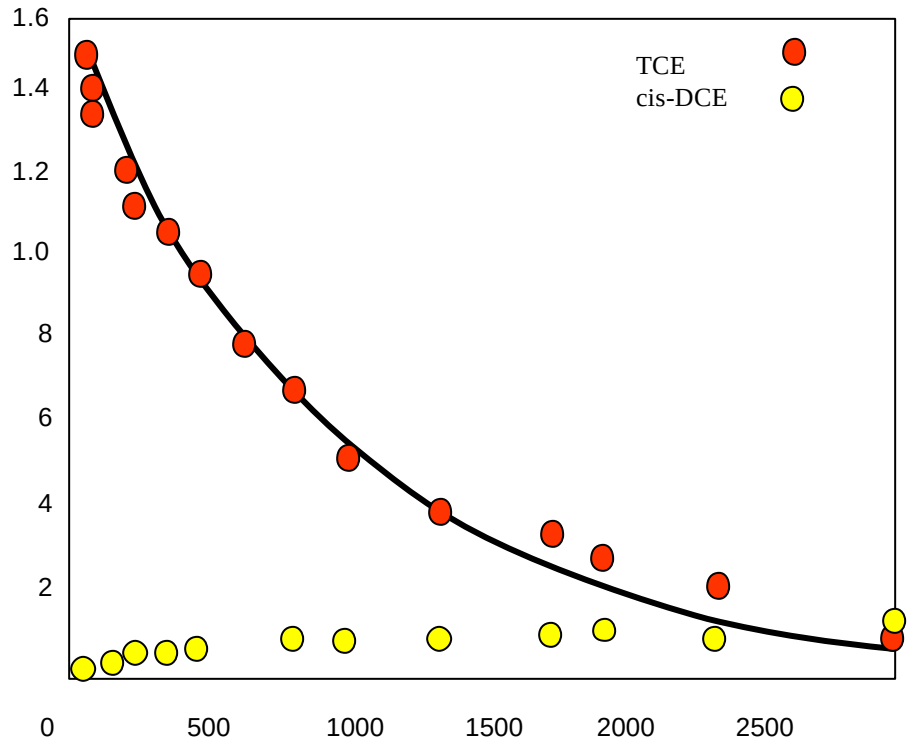
- Oxidation of soluble substrate (e.g., lactate) by common sulfate reducing bacteria generates H_2S
- H_2S reacts with abundant native Fe^{3+} minerals to make FeS

$$2FeOOH_{(s)} + 3HS^- \rightarrow 2FeS_{(s)} + S^o + H_2O + 3OH^-$$

- FeS is very reduced and reactive and spontaneously reduces chlorinated ethenes
  - Secondary abiotic dechlorination of TCE

$$4/9FeS + C_2HCl_3 + 28/9\ H_2O \rightarrow 4/9\ Fe(OH)_3 + 4/9SO_4^{2-} + C_2H_2 + 3Cl^- + 35/9H^+$$

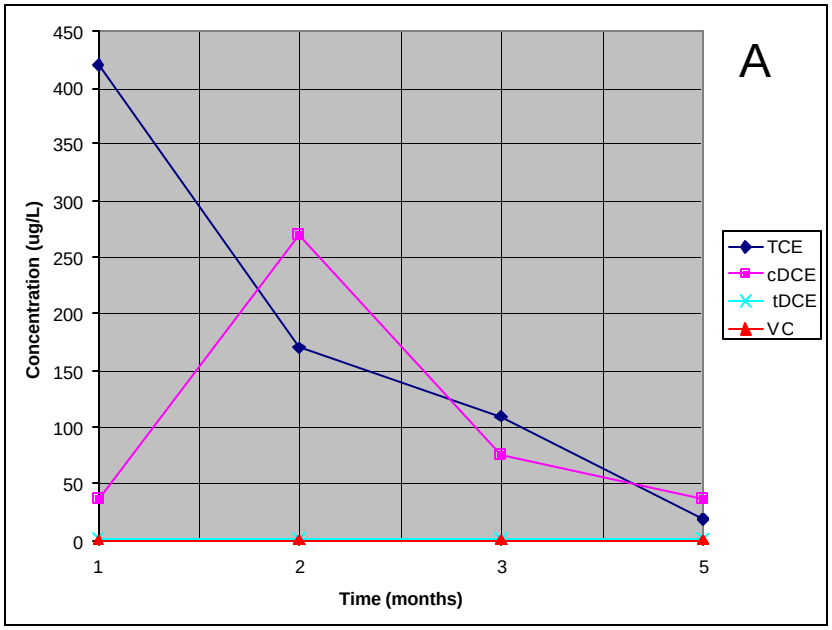
Abiotic TCE Dechlorination



- TCE dechlorinated abiotically by artificial FeS
- Fast rate (half life = 19 days)
- No daughter products

(Butler and Hayes, 1999)

Destruction of TCE via FeS

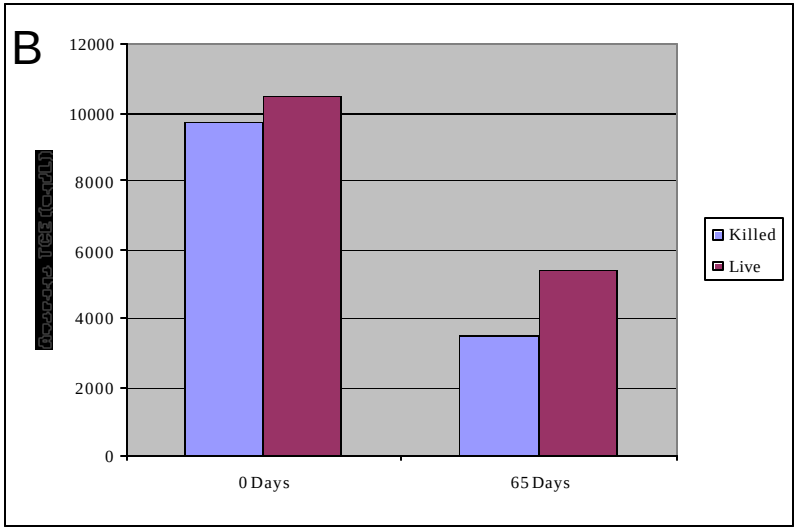


A) Artificial FeS mixed with Altus AFB sediment and TCE
(Terra Systems Study)

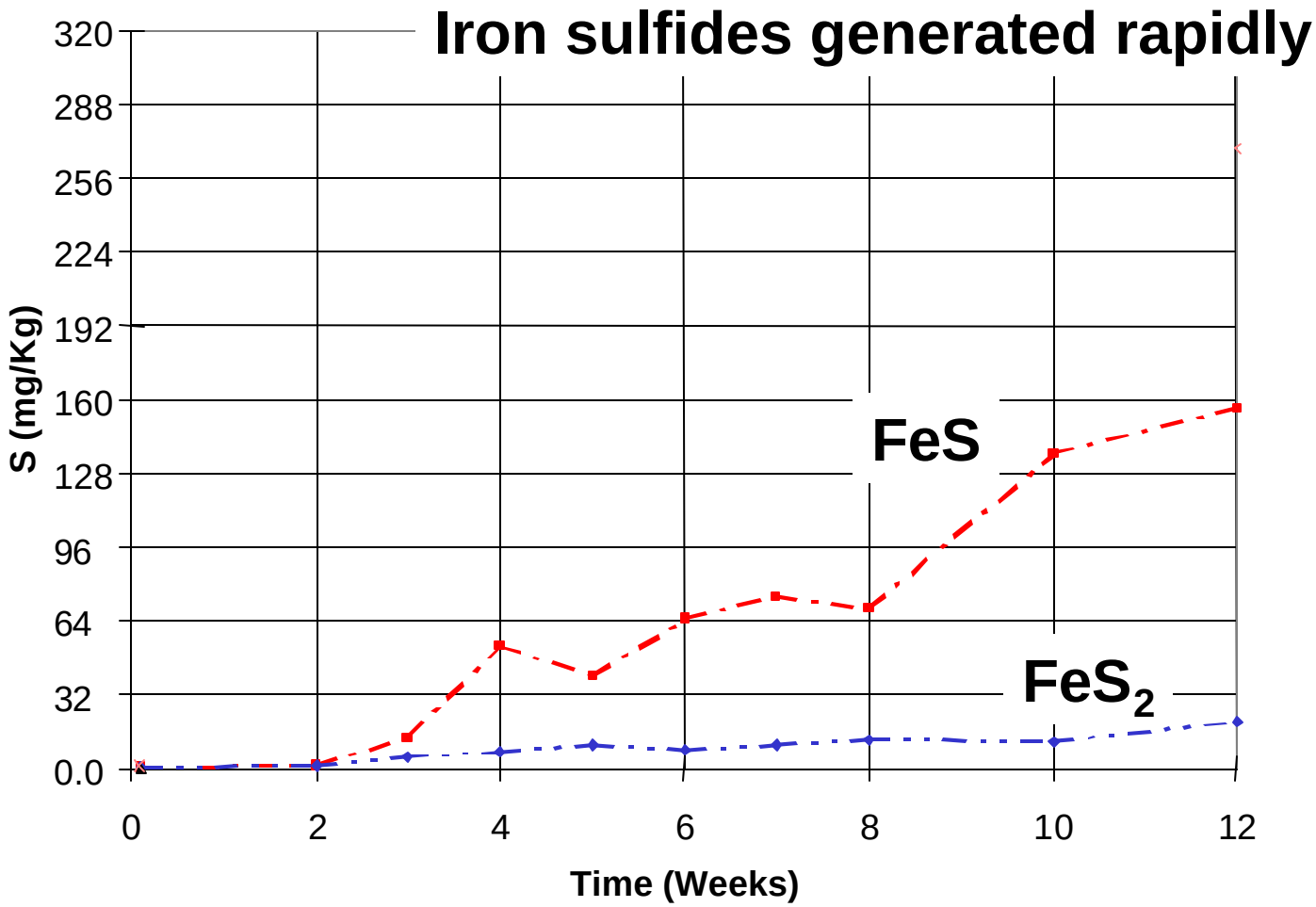
Half Life = 27 days

B) Removal of TCE in Altus AFB sediments with natural FeS.
(Rowan University Experiment ongoing)

Half Life = ~41 days



Microbial Production of FeS in Microcosm

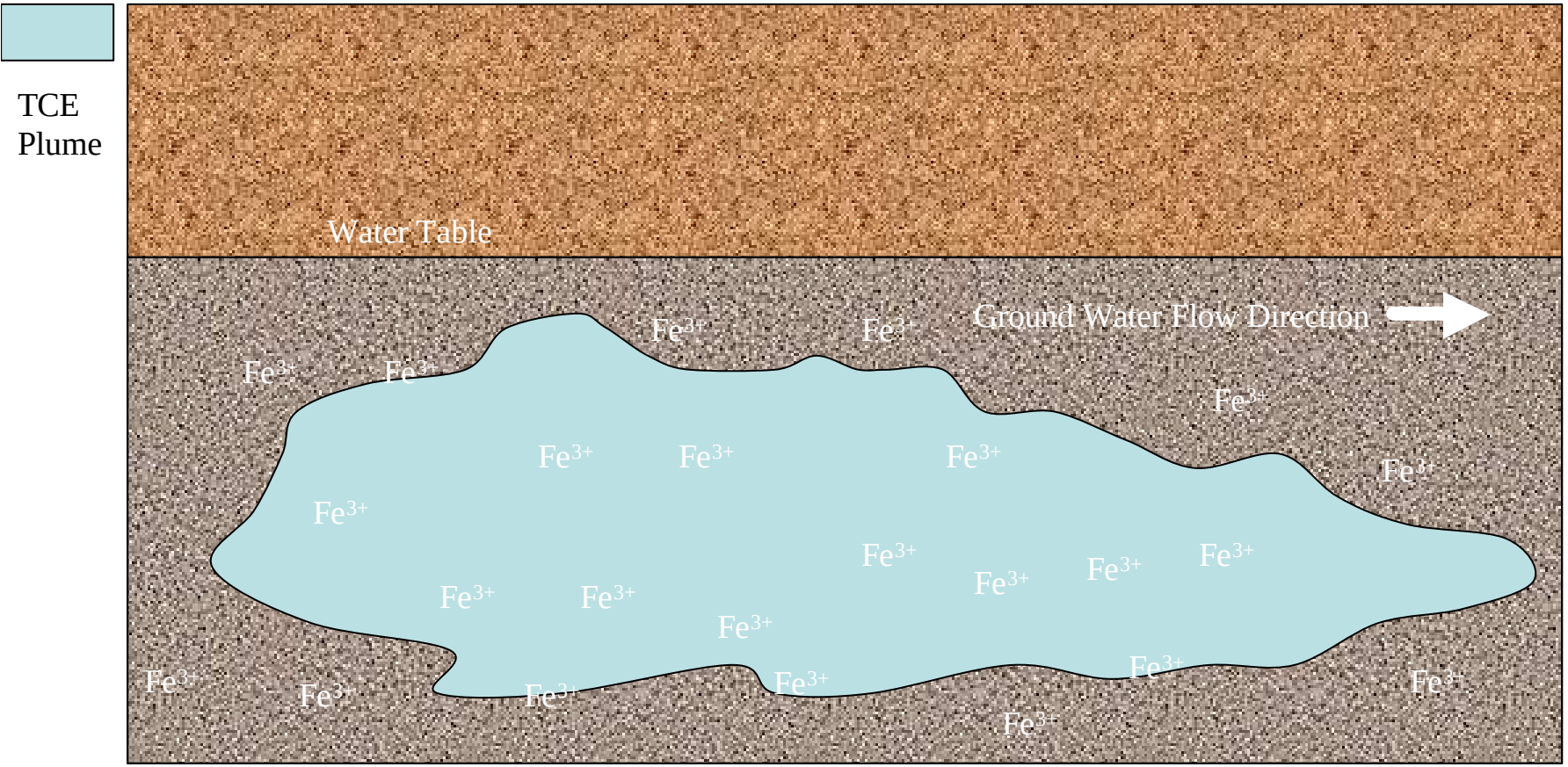


(Kennedy and Everett, 2001)

Abiotic TCE Reduction Characteristics

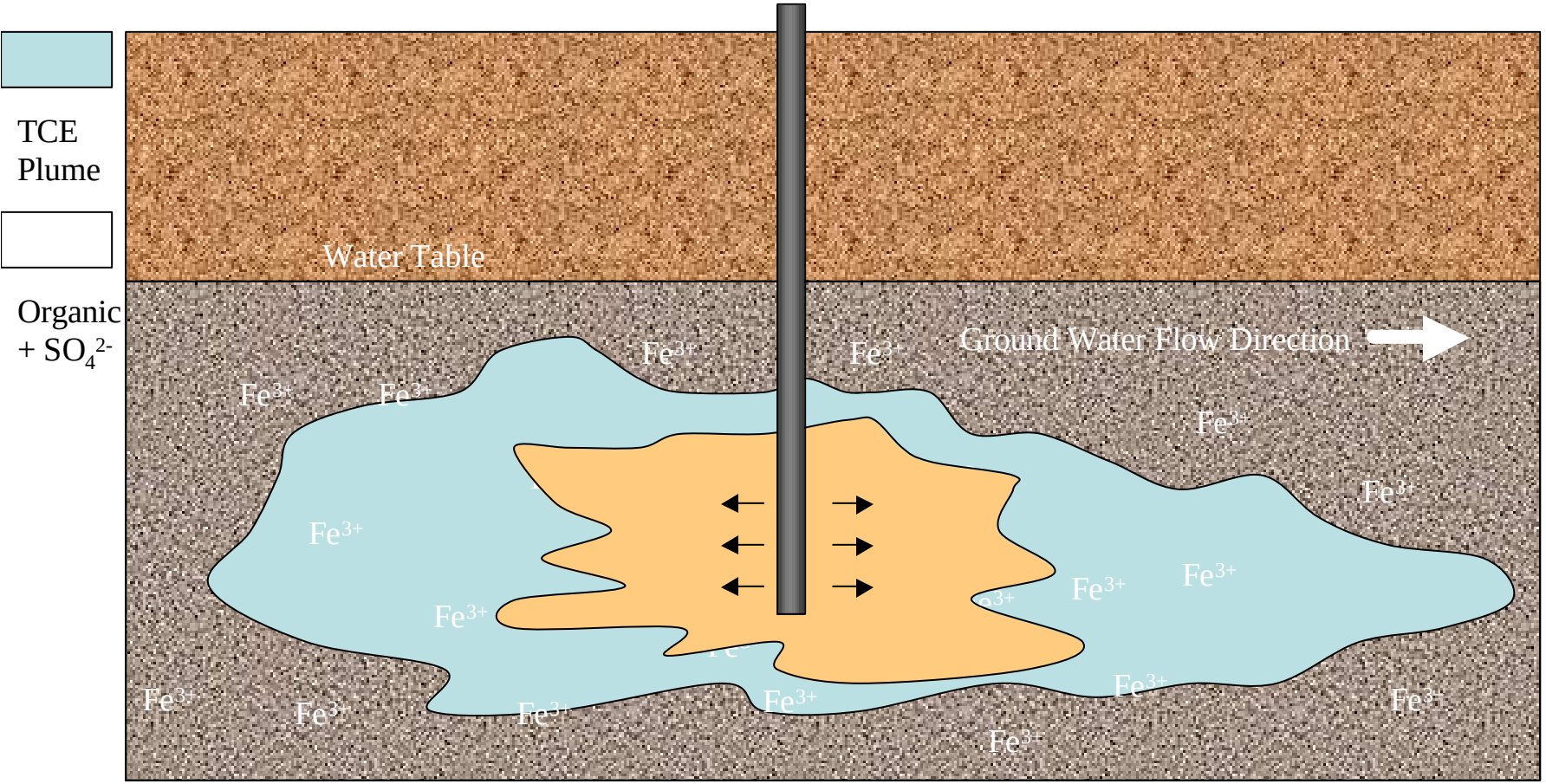
- Mineral FeS must be present
- Adequate concentrations of mineral Fe^{3+}, SO_4^{2-}, and organic needed to drive production of FeS
- Disappearance of chlorinated ethene without the buildup of daughter products

Theoretical Application of BiRD



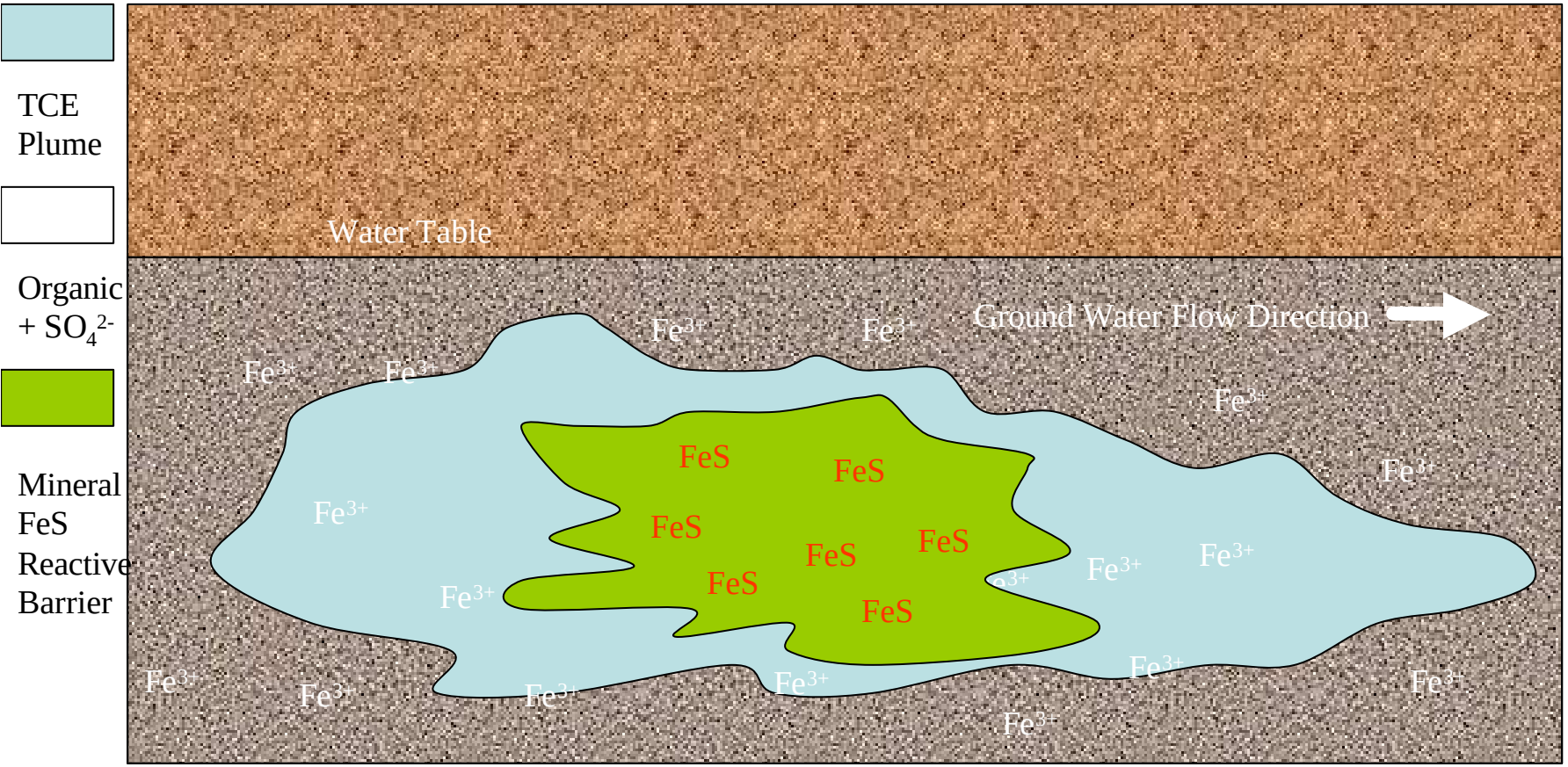
Aquifer Condition at preinjection with TCE contamination and native mineral Fe^{3+}. Sulfate may or may not be present in the system in sufficient quantities.

Theoretical Application of BiRD



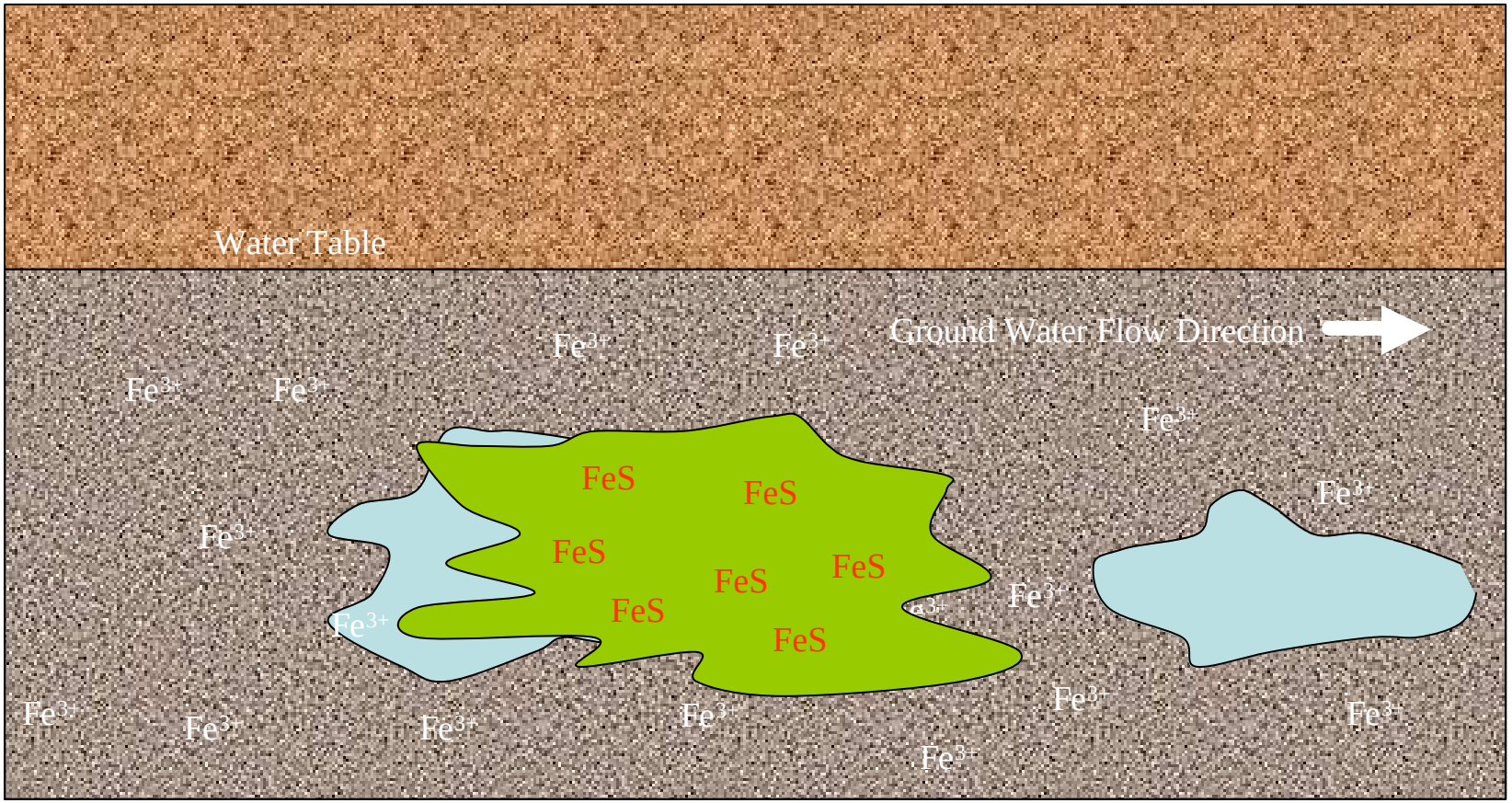
Injection points are installed in the aquifer and a solution of organic and sulfate (if needed) is introduced to the aquifer

Theoretical Application of BiRD



The injection point may be removed. FeS forms from oxidation of organic using SO_4^{2-} as electron acceptor. HS^- forms FeS by reaction with Fe^{3+}.

Theoretical Application of BiRD



TCE is reduced by FeS. TCE down gradient from FeS barrier is cut off from the source. Upgradient TCE is swept into the barrier and dechlorinated.

Theoretical Disadvantages of BiRD

- SO_4^{2-} may need to be added to subsurface but will be removed by microbial processes if sufficient organic added
- H_2S is generated but reacts with sediment

Theoretical Advantages of BiRD

- Reservoir permeability not affected
- Use of substrate for methanogenesis inhibited by electron acceptor competition with sulfate
- High sulfate environments augment rather than impede
- Sulfate reducing bacteria ubiquitous
  - bioaugmentation never necessary
- Rate of FeS production is rapid
- Rate of dechlorination is rapid
- Requirement for subsurface mixing reduced
- Deleterious byproducts not produced
  - Vinyl Chloride

The End

- Thanks for Your Attention!
- Thanks to AFCEE and Altus AFB

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